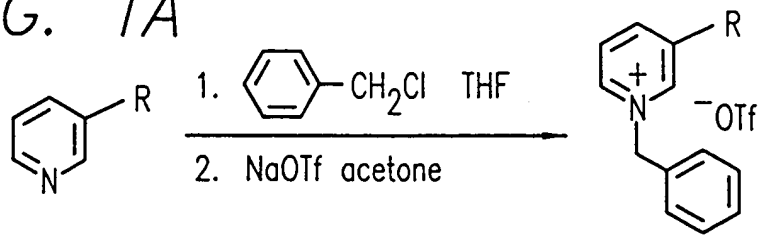
Serial No.: 09/805,725
Filed: March 12, 2001
Confirmation No. 4529
Attorney: Hana Verny (Reg. No. 30,518)
Telephone: (650)324-1677

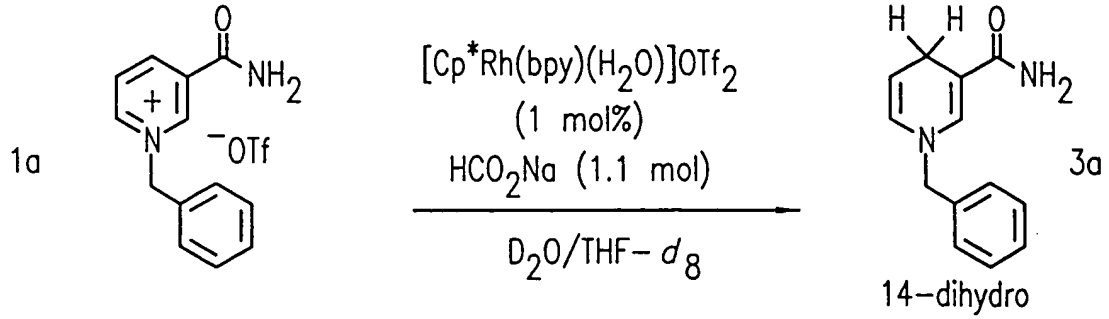
FIG. 1A



1a–i

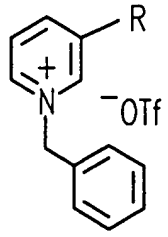
R=$-C(O)NH_2$ (1a);
$-C(O)NHCH_3$ (1b);
$-C(O)N(C_2H_5)_2$ (1c);
$-C(S)NH_2$ (1d);
$-C(O)CH_3$ (1e);
$-C(O)CCH_3$ (1f);
$-CN$ (1g);
$-CH_3$ (1h);
$-H$ (1i)

FIG. 1B



14–dihydro

FIG. 1C



(1)

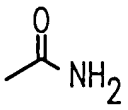
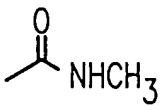
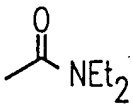
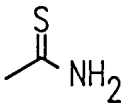
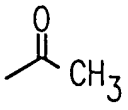
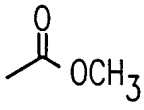
substrate	R	relative rate[A]	turnover/h[B]
1a		1.0	8
1b		0.9	8
1c		0.0	0
1d		1.3	11
1e		1.1	9
1f		1.3	11
1g	–CN	0.9	8
1h	$-CH_3$	0.0	0
1i	–H	0.0	0

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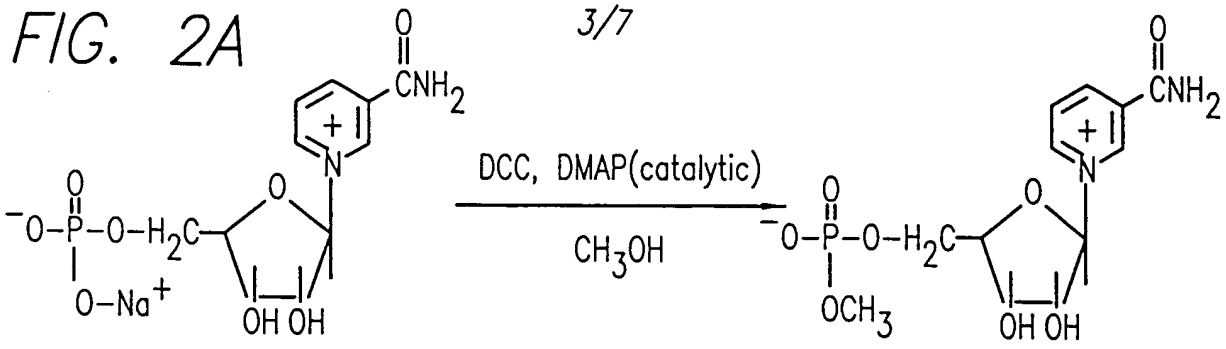
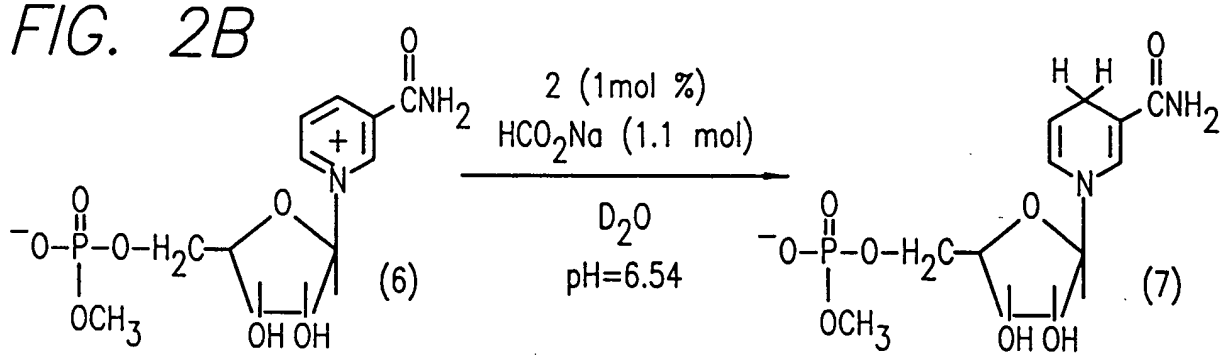
FIG. 2A



(5) (6)

FIG. 2B



(6) (7)

FIG. 3

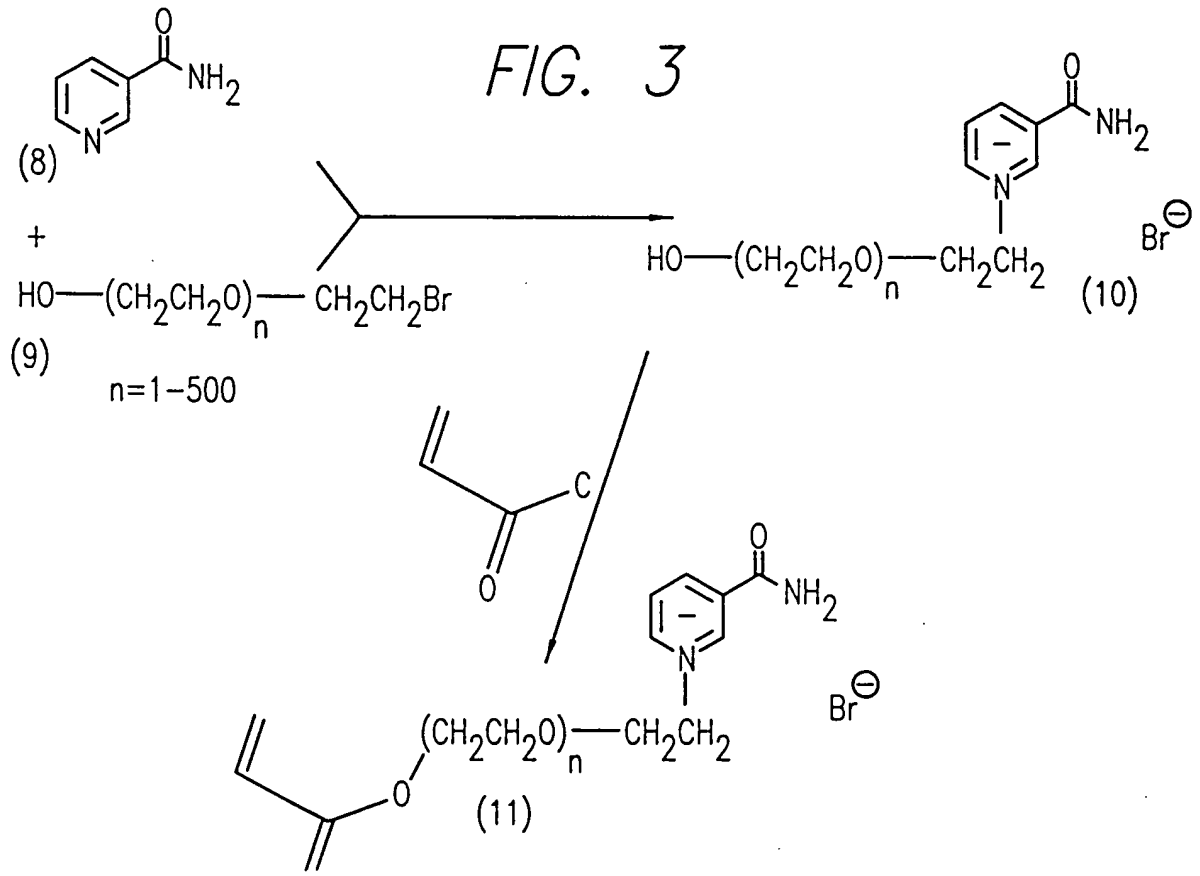
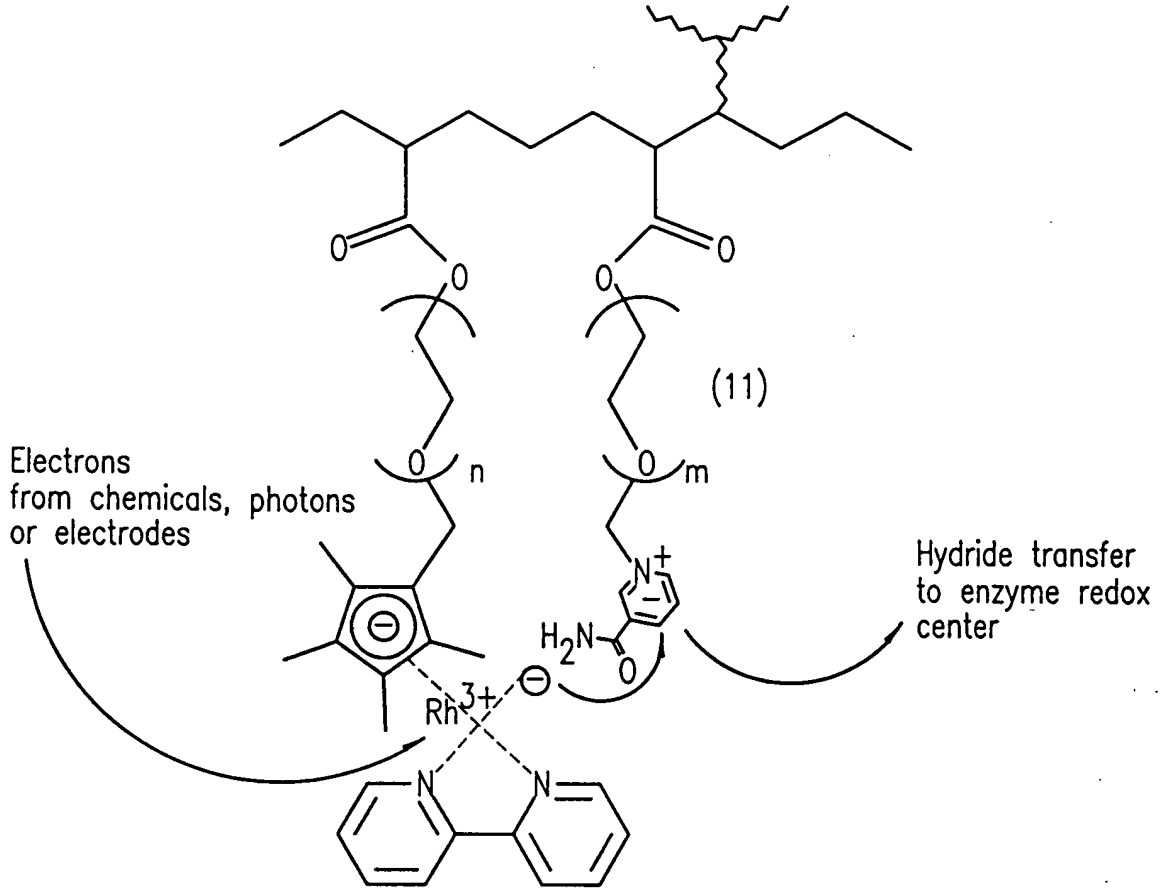


FIG. 4


(11)
Electrons
from chemicals, photons
or electrodes
Hydride transfer
to enzyme redox
center
Rh3+

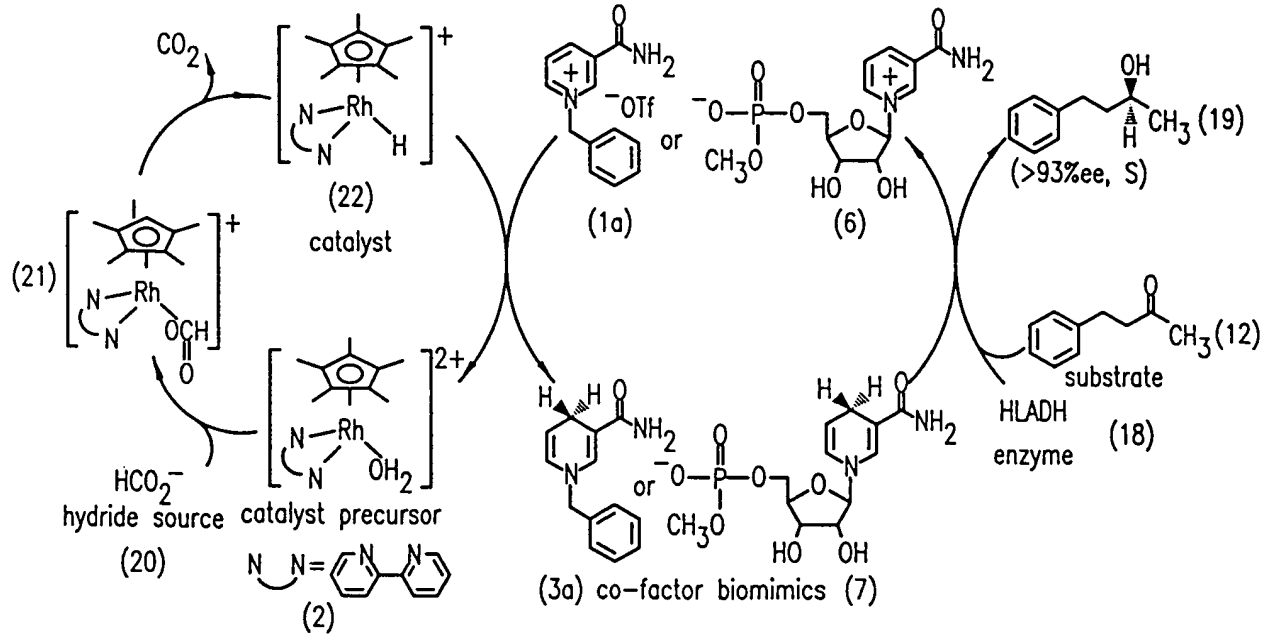
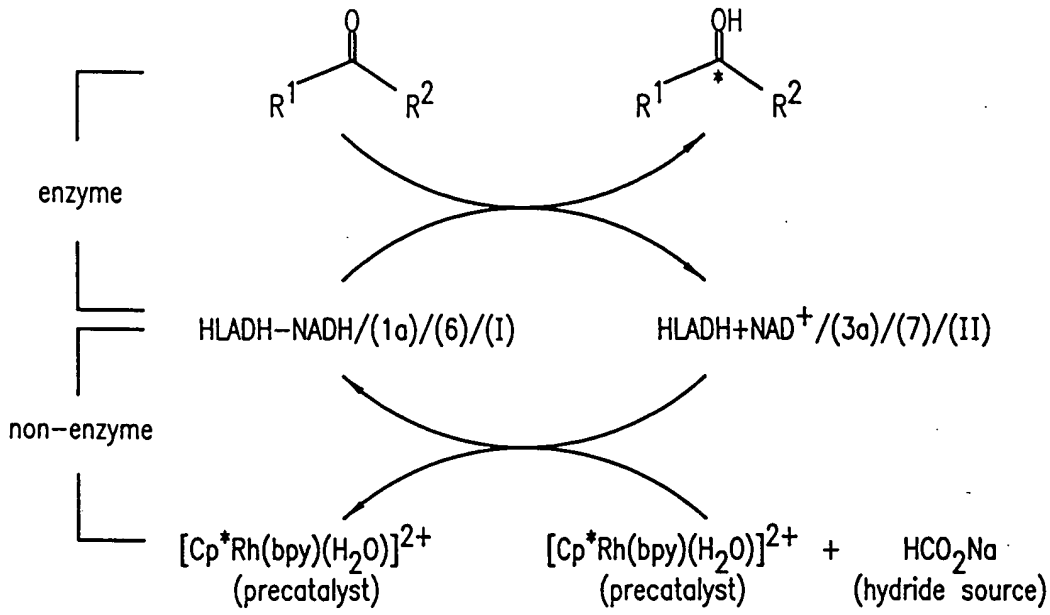
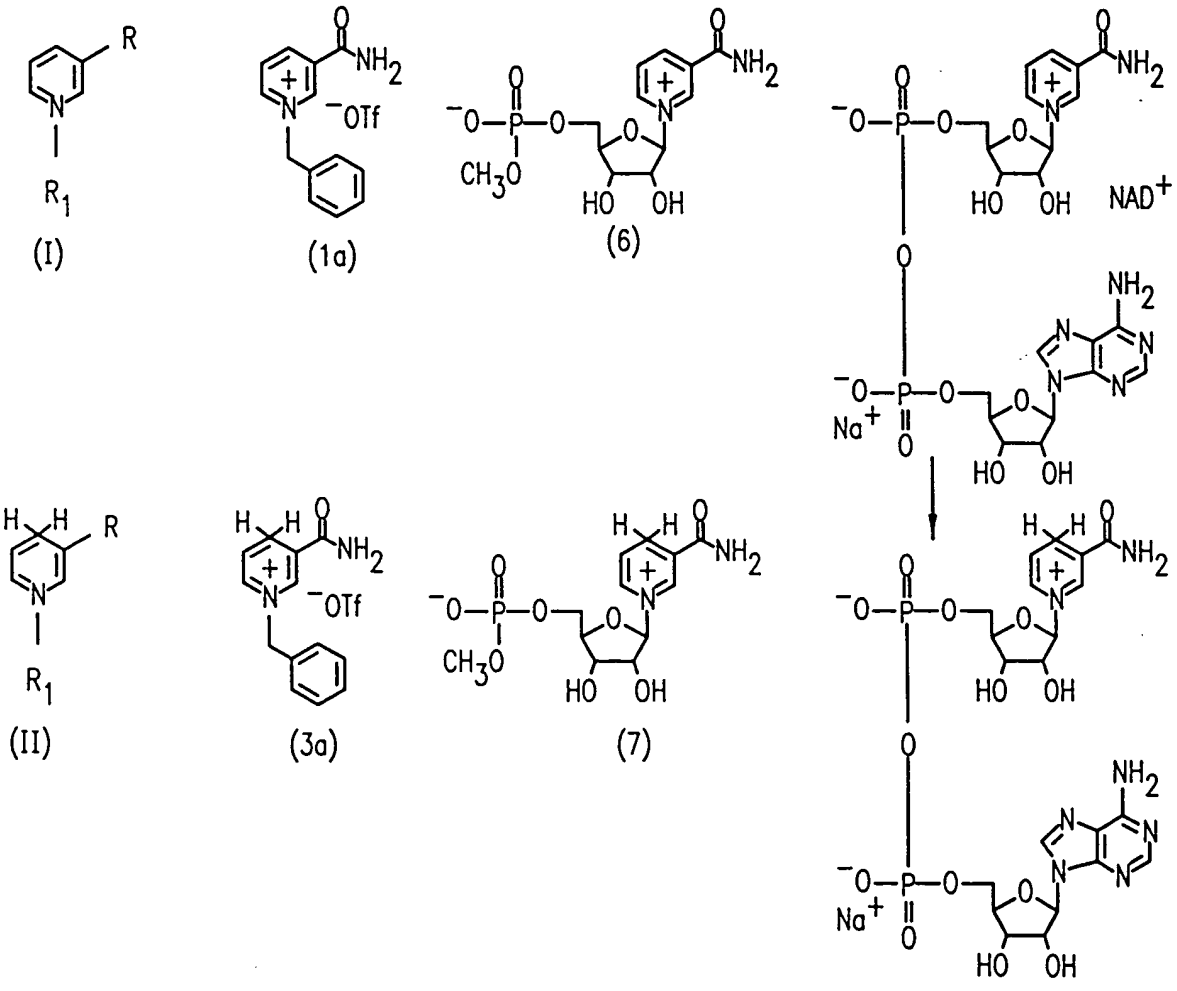

(22)
catalyst
(21)
(1a)
(6)
(19)
(>93%ee, S)
(12)
substrate
HLADH
enzyme
(18)
hydride source
(20)
catalyst precursor
(2)
(3a) co-factor biomimics (7)

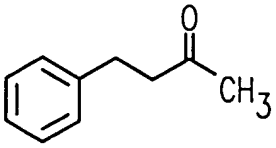
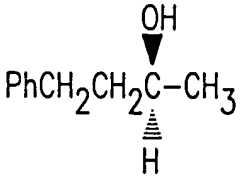
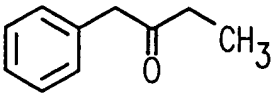
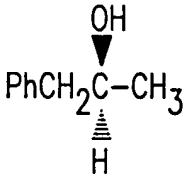
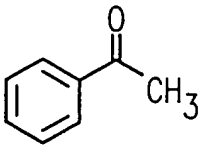
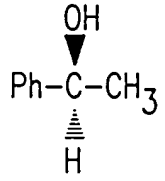
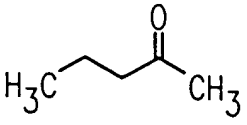
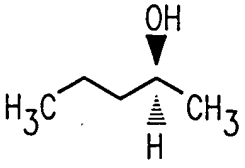
FIG. 6

Mimic NADH Models in Biocatalysis
Tandem Cofactor Regeneration, Enzyme Recognition and
Chiral Synthesis of Alcohols





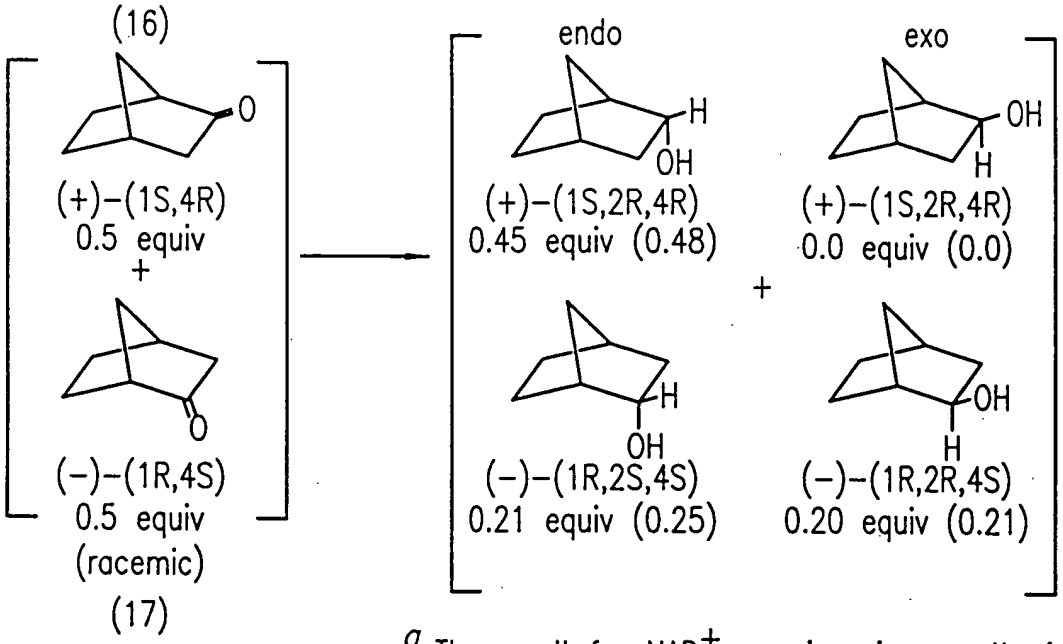
Enzymatic Reductions of Ketones with NAD^+ Models: Turnover Frequencies and Enantiomeric Excess[a,b]

substrate		product	% yield	TOF(d^{-1})	ee (%,S)
	12		90(91)	30(31)	93(93)
	13		55(59)	18(19)	>99(99)
	14		5(5)	4(4)	>96(96)
	15		41(59)	14(20)	85(85)[c]

[a]The results from NAD^+ were given in parenthesis. [b]The enantiomeric excess was determined by GLC with a modified β–cyclodextrin capillary column. [c]Based on derivatization with an optically pure isocyanate.

FIG. 7

Biomimetic Reduction of Norcamphor



[a] The result for NAD^+ was given in parenthesis.

FIG. 8

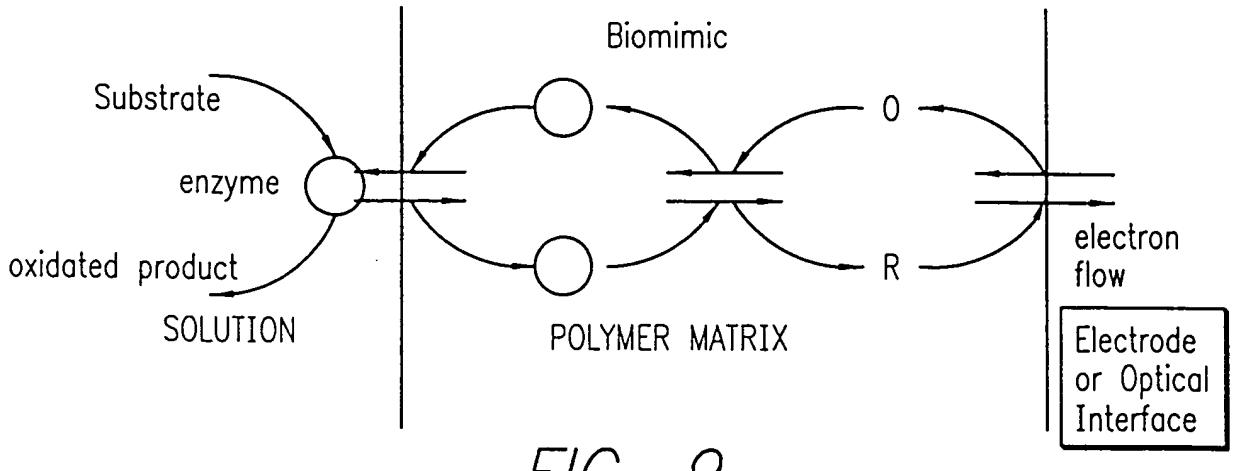


FIG. 9